

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization International Bureau



(43) International Publication Date  
29 September 2005 (29.09.2005)

PCT

(10) International Publication Number  
**WO 2005/089907 A1**

(51) International Patent Classification<sup>7</sup>: **B01D 53/22**,  
69/14, 71/60 // 179:00

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(21) International Application Number:  
PCT/NO2005/000098

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(22) International Filing Date: 18 March 2005 (18.03.2005)

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
20041199 22 March 2004 (22.03.2004) NO  
20041199 30 November 2004 (30.11.2004) NO

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

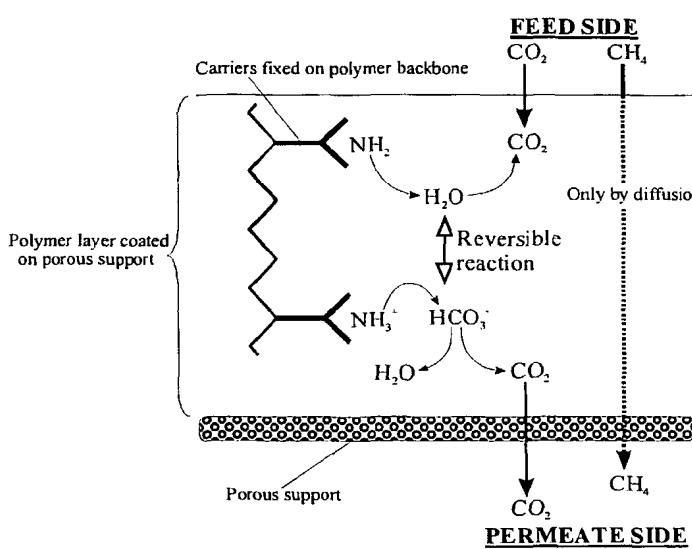
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Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: MEMBRANE FOR SEPARATING CO<sub>2</sub> AND PROCESS FOR THE PRODUCTION THEREOF



(57) Abstract: A fixed-site-membrane comprising a support structure coated with crosslinked polyvinylamine, wherein the crosslinking agent is a compound comprising a fluoride. The membrane comprises water, such as by being swelled in water vapour. A process for producing the membranes, and the use of such membranes for separation of carbon dioxide (CO<sub>2</sub>) from gas mixtures are disclosed.

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Title: Membrane for separating CO<sub>2</sub> and process for the production thereof

5    FIELD OF INVENTION

The present invention relates to novel fixed-site-carrier composite membranes and a process for producing the same, as well as the use of such membranes for separation of carbon dioxide (CO<sub>2</sub>) from gas streams.

10

BACKGROUND OF INVENTION

During the last couple of decades, concern for our global environment has brought into focus the need for CO<sub>2</sub> from anthropogenic sources being captured and brought into 15 storage. Industry will in the future have to comply with strict regulations on CO<sub>2</sub>-emissions, hence separation and recovery of CO<sub>2</sub> from gas streams have become of vital importance for industry from the viewpoint of environment and energy.

It is furthermore desirable to capture and separate CO<sub>2</sub> from various types of gas 20 streams like fuel gas, biogas, natural gas, synthesis gas and breathing etc. that constitute a part of all kind of combustions, petrochemical industry, biogas production and life support systems.

In general, CO<sub>2</sub> may be separated from gas mixtures of H<sub>2</sub>, CO, N<sub>2</sub>, O<sub>2</sub> and CH<sub>4</sub> by 25 reversible absorption methods employing various chemical and/or physical solvents. As the conventional process of treating and separating CO<sub>2</sub> is highly energy consuming, the cost as well as the increased demand of environmental protection bring about a need for new processes with energy efficient and more selective gas treating technology.

30    The use of a membrane for separation is suggested as a method consuming lower energy, see for example references 1 and 2 mentioned below.

A lot of research has been performed in order to obtain membranes having both high permeability and selectivity, as well as being stable and durable.

35

An approach to overcome the above limitations has been developed by casting carriers directly into the polymeric structure of the membranes. These so-called fixed-site-

carrier (FSC) membranes have carriers covalently bonded to the polymer backbone and the carriers have a restricted mobility.

CN-A-1363414 discloses the use of FSC membranes for the purpose of separating CO<sub>2</sub> from gases like N<sub>2</sub>, O<sub>2</sub>, CO and CH<sub>4</sub>. This publication discloses a process for preparing a composite membrane to separate carbon dioxide gas from a gas mixture by hollow or flat sheet membranes of polysulfone, polyacrylonitrile, or polyether sulfone through dipping the membrane in polyvinylamine solution for 5-60 minutes, cross-linking with 5-50 % glutaraldehyde solution for 5-40 minutes and in a solution of sulphuric acid or hydrochloric acid for 5-30 minutes, followed by drying and washing with water.

US 6,131,927 discloses a method for producing a composite gas separation membrane by treating the gas separation layer of the composite membrane with a treating agent that ionically bonds to the gas separation membrane layer of the treated composite membrane.

#### SUMMARY OF INVENTION

It has now surprisingly been found that the use of FSC membranes similar to those reported in CN-A-1363414 and varying the cross-linking agents, controlling the molecular weight and possibly swelling the membranes in water, results in a remarkable increase in selectivity for CO<sub>2</sub>/CH<sub>4</sub>, while the high permeability is maintained. The same high selectivity will be documented for CO<sub>2</sub> compared to gases with properties like that of CH<sub>4</sub>; i.e. N<sub>2</sub>, O<sub>2</sub>, CO.

It is an object of the present invention to provide membranes for the facilitated transport of CO<sub>2</sub>.

Another object of the invention is to provide membranes achieving both high permeabilities and high selectivities for CO<sub>2</sub> over gases like CH<sub>4</sub>, N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, CO.

Still another object of the invention is to provide such membranes, which are stable and durable.

These and other objects are achieved in a first aspect of the invention by a membrane comprising a support structure coated with crosslinked polyvinylamine, wherein the

crosslinking agent is a compound comprising fluoride. The membrane may also be swelled in water vapour.

In another aspect, the invention provides a process for producing a membrane as defined above, by preparing polyvinylamine with a predetermined molecular weight comprising a high degree of amination; coating said polyvinylamine on a support to obtain a membrane; crosslinking the membrane with a compound comprising fluoride; and possibly swelling the crosslinked membrane in water vapour.

10 In a further aspect, the invention comprises the use of a membrane as defined above, for separation of CO<sub>2</sub> from gas mixtures.

#### BRIEF DESCRIPTION OF THE DRAWINGS

15 Further objects, features and advantages of the invention will appear from the following description of several embodiments of the invention with reference to examples and the attached drawings in which:

20 Fig. 1 is a schematic diagram of an experimental setup for gas permeation measurement; Fig. 2 is a diagram over the effect of molecular weight of PVAm on ideal selectivity of CO<sub>2</sub>/CH<sub>4</sub>;

Fig. 3 is a schematic diagram over a proposed mechanism of facilitated transport in the fixed-site-carrier membrane;

25 Fig. 4 is a diagram over the influence of water on the permeation;

Fig. 5 is a schematic diagram over a proposed role of fluoride ion in facilitated transport;

Fig. 6 is a diagram over the effect of molecular weight of PVAm on permeance; and

Fig. 7 is a diagram indicating the possible effect of gas pressure on permeance.

30

#### DESCRIPTION OF EMBODIMENTS OF THE INVENTION

##### PREPARATION OF MEMBRANES

35 Fixed-site-carrier (FSC) membranes were prepared by coating or casting polyvinylamine (PVAm) on various supports such as flat sheet membranes of

polyethersulfone (PES), polyacrylonitrile (PAN), cellulose acetate (CA) and polysulfone (PSO). The PVAm cast on the support was crosslinked by various methods using glutaraldehyde, hydrochloric acid, sulphuric acid and ammonium fluoride. The effect of molecular weight of PVAm and feed pressure on the permeance and selectivity  
5 was also investigated. The permeance and selectivity of the membranes were measured in water vapour swollen conditions.

#### Acrylamide polymerization

The polymerization of acrylamide ( $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}_2$ ; Merck) was carried out  
10 according to well-known procedures (see reference 3, below) using ammonium persulfate ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ) and sodium sulphite ( $\text{Na}_2\text{SO}_3$ ) as initiators. Persulfate was decomposed by sulphite ion as the reducing agent, and the polymerization included the three basic steps; initiation, chain propagation and chain termination. The polymerization was allowed to proceed at 45°C for 5 h and 55°C for 2 h. The molecular weight of the resulting polyacrylamide (PAA) was determined by measuring the  
15 viscosity of the diluted polymer solution. The intrinsic viscosity of PAA in water was determined by using an Ubbelohde viscometer.  
PAA with different molecular weight could be obtained by controlling the concentration of initiators. The obtained PAA solution was pale yellowish, but clear and very viscous,  
20 which depended on molecular weight and concentration of PAA.

#### Preparation of polyvinylamine by Hofmann reaction of polyacrylamide

The Hofmann reaction was suggested as a quick and convenient method of preparing PVAm from PAA by Tanaka et al. (see references 5-7). After examination and extent  
25 investigation of Hofmann reaction, Archari et al. (see reference 4) proposed that PVAm could be prepared from PAA by the Hofmann reaction with a high degree of amination (meaning more than 90 %) keeping the extent of side reactions to a low level by careful control of reaction parameters. The amino group content in PVAm was measured to be over 90 mole %. The obtained product was a hygroscopic white solid. The final  
30 polymer was dissolved in water to a suitable concentration (5-10%) for membrane casting. The average molecular weight of PVAm was determined by the following relation:  $[\eta]/(\text{dL}\cdot\text{g}^{-1}) = 6.2 \cdot 10^{-3} M_n^{0.88}$  where  $[\eta]$  is the intrinsic viscosity in 0.01 M aqueous NaOH/0.1 M aqueous NaCl water at 25°C (see references 4 and 7).

35 Main reaction:  $\text{R}-\text{CO}-\text{NH}_2 + \text{NaOCl} + 2 \text{NaOH} \rightarrow \text{RNH}_2 + \text{Na}_2\text{CO}_3 + \text{NaCl} + \text{H}_2\text{O}$

Membrane preparation

Two microporous polysulfone flat sheet support structures or membranes (PSO) were tested: one with a molecular weight cut-off (MWCO) of 20,000 (from Danish Separation Systems AS (DSS)) and one with MWCO of 30,000 (from Osmonics Vista Operation). The following supports were also tested: polyethersulfone (PES, MWCO 10,000) cellulose acetate (CA, MWCO 20,000) and polyacrylonitrile (PAN, MWCO 75,000) (all three from Osmonics Vista Operation).

The support membrane was cut into suitable pieces and taped to a clean, levelled glass plate. The casting polymer solution of PVAm was poured on the support, and film thickness adjusted by using a casting knife. The gap between the casting knife and the support membrane was set to approximately 20 $\mu\text{m}$  – thinner membranes can be made by adjusting the casting knife. The casting polymer solution was evaporated at room temperature for at least 6 h.

A layer of PVAm (MW ~34 000) was clearly formed on the polysulfone membrane from DSS having a MWCO of about 20,000. The thickness of the layer was about 5-10  $\mu\text{m}$ ; hence some of the solution had sifted down into the support.

Meanwhile the PVAm (MW 39 000) layer was hardly visible for membranes coated on polysulfone membranes from Osmonics (MWCO=30,000). It was observed that the PVAm sifted down into the support membrane and below the membrane, probably because of the fact that the molecular weight of the PVAm was too low for the pores of the membrane. Consequently, there should be a reasonable difference between the average molecular weight of PVAm and the molecular weight cut-off of the support structure. Such a difference may be larger than about 10,000, such as larger than about 15,000, for example larger than about 20,000. In this case, it is also possible to obtain and maintain a defectfree dense layer of the selective PVAm membrane or layer. Any voids or openings in the PVAm layer of the membrane will disturb the selection properties of the membrane.

The dried cast membranes were crosslinked by different procedures:

- (1) Glutaraldehyde (50%, 30 min);
- (2) Glutaraldehyde (50%, 30 min), and then H<sub>2</sub>SO<sub>4</sub> (pH=1, 10-30 min);
- (3) NH<sub>4</sub>F (0.5M, 2 h);
- (4) Glutaraldehyde (50%, 30 min), and then NH<sub>4</sub>F (0.5 M, 2 h);

(5) H<sub>2</sub>SO<sub>4</sub> (pH=1, 10-30 min) or HCl (pH=1, 10-30).

Procedure (2) above, is according to the crosslinking disclosed in CN-A-1363414.

5 Care was taken to ensure that the membrane was levelled during drying and crosslinking processes in order to obtain an even and defect-free membrane. The crosslinked membranes were stored in a chamber saturated with water vapour.

10 Another method of producing a permselective membrane permeable and selective for CO<sub>2</sub> may be the following: A bundle of hollow fibres of a suitable support structure material, as those mentioned above, is formed. A layer of PVAm is formed at the outside of each hollow fibre by immersing the fibres in a bath comprising a solution of PVAm. After some time, the bundle of hollow fibres is removed and allowed to dry at room temperature for at least 6 hours. Thus, a layer of PVAm was formed at the outside 15 of each hollow fibre. The PVAm was then crosslinked by the procedures described above.

#### Membrane testing

20 Permeability of the membranes was measured with an apparatus equipped with a humidifier, see Fig. 1.

Fig. 1 shows an experimental setup for gas permeation measurements. The chosen gases may be mixed in any ratios in a gas flow line A, in which flow, pressures and temperature are controlled. The gas mixture is lead to humidifiers in tanks 1 where it bubbles through water, and then to a membrane separation cell 2. Either the retentate stream C, or the permeate stream E, may be lead to a gas chromatograph (GC) 4 for analysis of the composition. The gas is dried by desiccator 3 before going to the GC. Helium is used as carrier gas. The various gas flows are controlled by valves V1 to V12. Moreover, the abbreviations FI, FC, PI and PC in circles are flow indicator (FI), flow controller (FC), pressure indicator (PI) and pressure controller (PC), respectively.

A membrane was placed on a porous metal disk in a flat type membrane cell 2 and was sealed with rubber O-rings.

35 All experiments were conducted in a constant temperature environment and the experiment temperature range was between 25-35°C and the pressure difference between the feed and the permeate sides was 2-4 bar.

The permeance (flux) was calculated as P/l in the unit m<sup>3</sup> (STP)/(m<sup>2</sup> bar h). The flux was found to be strongly dependent on the thickness of the membrane. For the membranes reported herein, the thickness was ~20μm. When the thickness is brought down to at least 1/10 of this, permeation is expected to increase correspondingly by 10 times.

Permselectivity results of PVAm membranes cast on different support materials are compared in Table 1. As can be seen, PSO supported membranes showed much higher selectivity of CO<sub>2</sub> over CH<sub>4</sub>. CA, PAN and PES supported membranes showed high permeance, but their selectivity was small. Osmonics PSO which had no visible PVAm layer showed lower permeance as well as lower selectivity than DSS PSO. The DSS PSO support seemed to be the most suitable support for the composite membrane and was therefore chosen in the further investigations.

15

**Table 1**Comparison of membranes on different support materials in permselectivity<sup>a,b</sup>

Support	Polysulfone (DSS)	Polysulfone (Osmonics)	Cellulose acetate	Polyacrylo- nitrile	Polyether- sulfone
CO <sub>2</sub> permeance <sup>c</sup>	0.00837	0.0063	0.099	0.0327	0.00388
α (CO <sub>2</sub> /CH <sub>4</sub> )	1143	26.9	17.3	5.1	6.5

<sup>a</sup>Membrane preparation: Cast PVAm solution on supports, dried at room temperature, crosslinked with NH<sub>4</sub>F, stored in chamber saturated with water vapour.

20 <sup>b</sup>All the data measured at 2 bar and room temperature.

<sup>c</sup>Permeance, P/l, in units of m<sup>3</sup> (STP)/m<sup>2</sup> bar h.

The results according to Table 1 may be explained as follows: The crosslinking with NH<sub>4</sub>F was possibly more easily performed on a support structure where the difference of the MWCO for the support and the MW of the PVAm were equal to or higher than about 20,000. This may explain the difference between the PSO from DSS, Osmonics and the PES; CH<sub>4</sub> is more efficiently withheld where the crosslinking has been successful. It appears to be difficult to form and crosslink a selective layer both on CA and PAN. Thus, it seemed to be difficult to restrict the permeation of CH<sub>4</sub>. The flux and selectivity shown for CO<sub>2</sub> using these two materials for support, show that an effective selective film was not formed on the top.

For the same crosslinking condition, an increase in molecular weight of polyvinylamine resulted in a significant decrease in permeation for CH<sub>4</sub> and a remarkable increase in the selectivity as shown in Fig. 6. This corresponds clearly to molecular weight, and when this was more than 70,000, the increase of selectivity was remarkable. This is shown in 5 Fig. 2 where the effect of molecular weight of PVAm on ideal selectivity of CO<sub>2</sub>/CH<sub>4</sub> at 35°C, 3 bar, is plotted. The membrane preparation used in this experiment is cast PVAm solution on DSS PSO, dried at room temperature, and crosslinked with NH<sub>4</sub>F.

The PVAm/PSO membranes were tested for two months and did still maintain the high 10 selectivity of CO<sub>2</sub>/CH<sub>4</sub>.

The results of different crosslinking methods are shown in Table 2. Among the five crosslinking methods, the crosslinking with NH<sub>4</sub>F resulted in a surprisingly high selectivity.

15

**Table 2**

Comparison of methods of crosslinking in permselectivity for PVAm membranes cast on PSO support<sup>a,b</sup>

Method of crosslinking	H <sub>2</sub> SO <sub>4</sub>	HCl	NH <sub>4</sub> F	Glutaraldehyde + H <sub>2</sub> SO <sub>4</sub> (CN-A-1363414)	Glutaraldehyde + NH <sub>4</sub> F
CO <sub>2</sub> permeance <sup>c</sup>	0.00567	0.00755	0.00837	0.00321	0.0372
$\alpha$ (CO <sub>2</sub> /CH <sub>4</sub> )	19.0	13.5	1143	21.6	12.0

<sup>a</sup>Membrane preparation: cast PVAm solution on DSS PSO, dried at room temperature, crosslinked with 20 different methods, stored in chamber saturated with water vapour.

<sup>b</sup>All the data measured at 2 bars and room temperature.

<sup>c</sup>Permeance, P/l, in units of m<sup>3</sup> (STP)/m<sup>2</sup>bar hr.

The membrane crosslinked by ammonium fluoride showed the best results and the ideal 25 selectivity of CO<sub>2</sub>/CH<sub>4</sub> was over 1000. This was a much unexpected result.

In order to obtain the carrier effect for CO<sub>2</sub>, the membrane of the present invention should comprise water, such as being kept wet, such as swollen with water vapour. The proposed carrier mechanism in the wetted membrane is shown in Fig. 3. It was observed 30 a decrease in permeance when membrane was allowed to dry out, while the original conditions were restored when the membrane again was wetted, see Fig. 4.

The present invention comprises membranes having a support structure wherein the MWCO is from about 20,000 to about 40,000 such as from about 20,000 to about 30,000. The preferred support structure is PSO.

5

The membranes further comprise PVAm of high molecular weight. In a preferred embodiment the molecular weight is higher than 70,000.

The preferred crosslinking agent of the membranes according to the present invention is 10 NH<sub>4</sub>F. To serve as a crosslinking agent also other compounds containing fluoride may be used according to the present invention. Examples of other fluoride containing compounds are ammonium bifluoride (NH<sub>4</sub>HF<sub>2</sub>) and hydrofluoric acid (HF).

Without being bound by the following theory, we believe that the use of a fluoride ion 15 may be of benefit of two reasons. The possible role of fluoride ions in facilitated transport in a swollen membrane, is illustrated in Figure 5. The water molecule becomes more basic than pure bulk water when it is hydrogen bonded to a fluoride ion, and the fluoride is creating highly polar sites in the membrane. The basic water molecule has an increased affinity for CO<sub>2</sub> that leads to increased concentration of HCO<sub>3</sub><sup>-</sup> in the 20 membrane and a consecutively increased transport of CO<sub>2</sub>. The permeation of gases like CH<sub>4</sub>, N<sub>2</sub>, and O<sub>2</sub> will on the other hand be blocked by the highly polar sites in the membrane because of low solubility of these nonpolar gases, and an increased 25 selectivity may arise. The characteristics of a facilitated or carrier-mediated transport are the occurrence of a reversible chemical reaction or complexation process in combination with a diffusion process. This implies that either the diffusion or the 30 reaction is rate limiting: For the membrane in the current study, the diffusion is assumed to be rate limiting. The total flux of a permeate A (here CO<sub>2</sub>) will thus be the sum of both the Fickian diffusion and the carrier-mediated diffusion. The nonpolar gases in the gas mixture will exclusively be transported through the membrane by Fickian diffusion. 35 It can be shown that the driving force over the membrane will be the difference in partial pressures for the Fickian diffusion, and that transport also will depend on the solubility coefficient for the gas in the polymer. For the carrier-mediated transport, the driving force will be the concentration difference of the complex AC over the membrane. The permeation of the nonpolar gases may additionally be hindered because of the highly polar sites in the membrane caused by the presence of fluoride ions. This should then lead to an increased permeance of CO<sub>2</sub> compared to gases like CH<sub>4</sub>, N<sub>2</sub>, and O<sub>2</sub>, giving high selectivities in favor of CO<sub>2</sub>.

10

Since the partial pressure difference of CO<sub>2</sub> over the membrane is of importance for the flow, the effect of feed gas pressure on the permeance of CO<sub>2</sub> and CH<sub>4</sub> in a PVAm/PSO membrane were studied, see Fig. 7. In the range of 2–4 bar, the permeance of CO<sub>2</sub> was almost maintained. This could indicate that the carrier sites for CO<sub>2</sub> became saturated as  
5 pressure increased, and that transport because of the solution–diffusion mechanism became more important. The net result would be no change. The permeance of CH<sub>4</sub> increased slightly, most likely because of enhanced sorption according to the solution–diffusion mechanism. A slight decrease in selectivity resulted with increased pressure.

10 The gas passing over the membrane to the permeate side should be removed as much as possible to maintain the concentration gradient over the membrane.  
In general the thickness of selective PVAm layer on the membrane should be as thin as possible in order to increase flux of carbon dioxide through the layer and membrane.  
The thickness may be < 15 µm, such as < 10 µm, or even < 5 µm, or for example < 2  
15 µm.

In order to keep the membrane wet, the construction of the membrane module is of importance. The membranes according to the present invention may be prepared as a flat sheet type membrane or composite hollow fibres.

20 When using the membranes of the present invention for separation of CO<sub>2</sub>, the process temperature may be kept below the boiling point, T<sub>b</sub>, for water at operating pressure.

To avoid compaction of the membranes of the present invention, the pressure drop  
25 across the membrane, ΔP, may be below 80 bar.

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## CLAIMS

1.  
5 A membrane comprising a support structure coated with crosslinked polyvinylamine, wherein the crosslinking agent is a compound comprising a fluoride.
2.  
10 The membrane according to claim 1, wherein the polyvinylamine comprises water.
3.  
15 The membrane according to claim 1 or 2, wherein the polyvinylamine of the membrane is swelled by water vapour or a water containing diluent.
4.  
20 The membrane according to claim 1, 2 or 3, wherein the support structure is a flat sheet membrane or a hollow fibre membrane.
5.  
25 The membrane according to claim 1, wherein the support structure is a membrane having a molecular weight cut-off in the range of from about 20,000 to about 40,000.
6.  
30 The membrane according to any one of claims 1 – 5, wherein the support structure is a membrane having a molecular weight cut-off which is about 10,000, such about 15,000, for example about 20,000, less than the molecular weight of the polyvinylamine.
7.  
35 The membrane according to any one of the previous claims, wherein the support structure is made of polysulfone.
8.  
35 The membrane according to any one of the previous claims, wherein the molecular weight of said polyvinylamine is above about 30,000, such as above about, 50,000, for example above about 70,000 or even above 100,000.

9.

The membrane according to claim 8, wherein the molecular weight of said polyvinylamine is below about 150,000.

5

10.

The membrane according to any one of the previous claims, wherein the crosslinking agent is selected from the group comprising: ammonium fluoride, ammonium bifluoride, and hydrofluoric acid.

10

11.

The membrane according to claim 10, wherein the crosslinking agent is ammonium fluoride.

15

12.

A process for producing a membrane according to any one of the previous claims, comprising:

20

- preparing polyvinylamine;
- coating said polyvinylamine on a support structure to obtain a membrane;
- crosslinking the polyvinylamine of the membrane with a compound comprising a fluoride.

25

13.

The process according to claim 12, further comprising:

- swelling said polyvinylamine of said membrane by exposing said polyvinylamine for water vapour or a water containing diluent.

30

14.

The process according to claim 12 or 13, wherein the polyvinylamine has a molecular weight above about 30,000, such as above about, 50,000, for example above about 70,000.

35

15.

The process according to claim 12, 13 or 14, wherein the molecular weight of said

polyvinylamine is below about 150,000.

16.

Use of a membrane according to any one of claims 1 to 11, for separation of CO<sub>2</sub> from gas mixtures.

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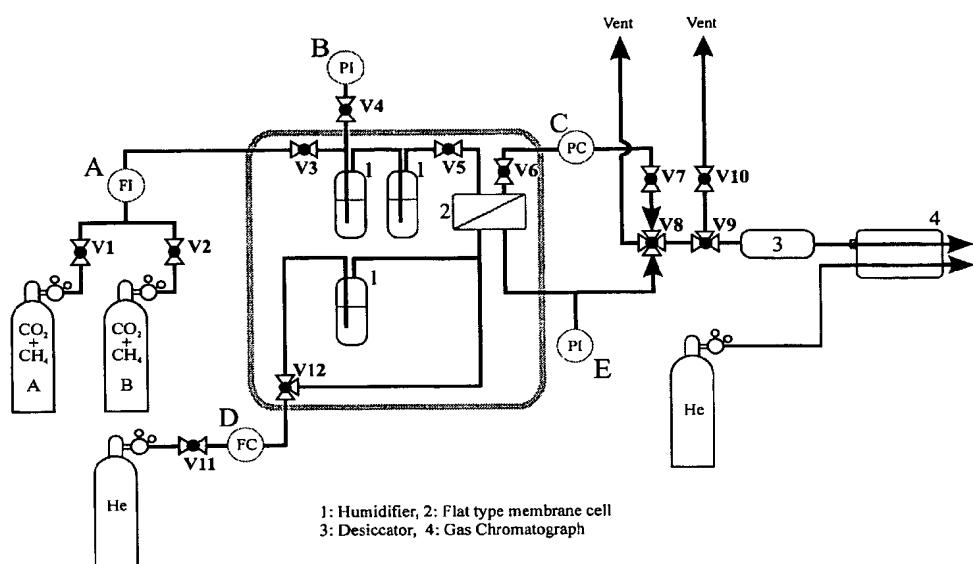


Fig. 1

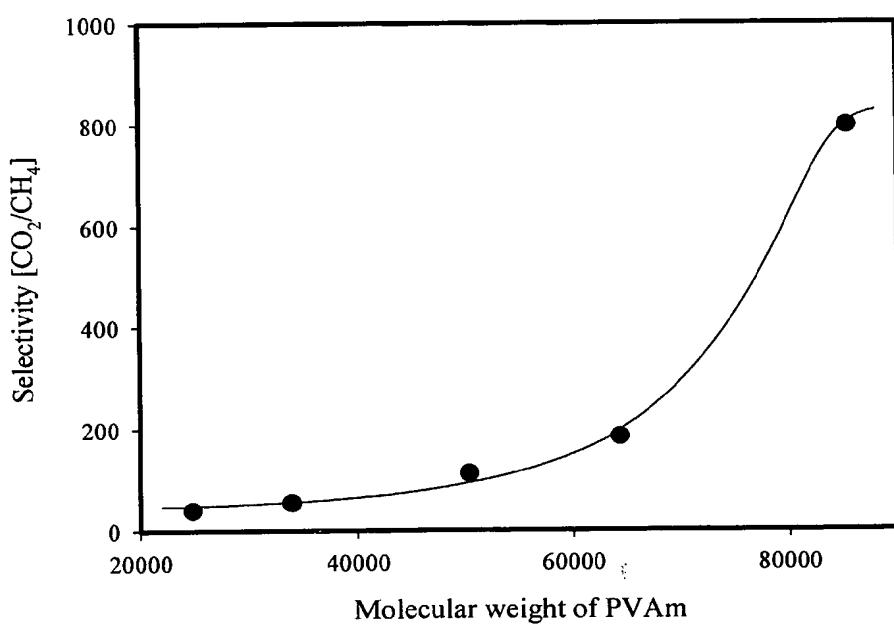


Fig. 2

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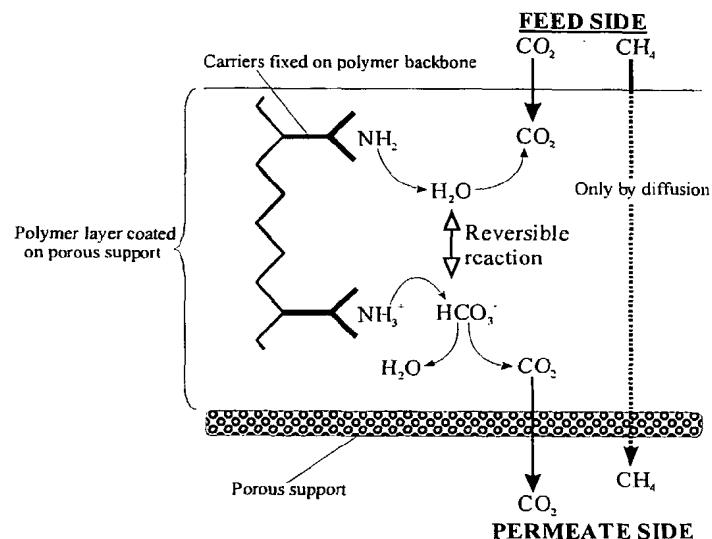
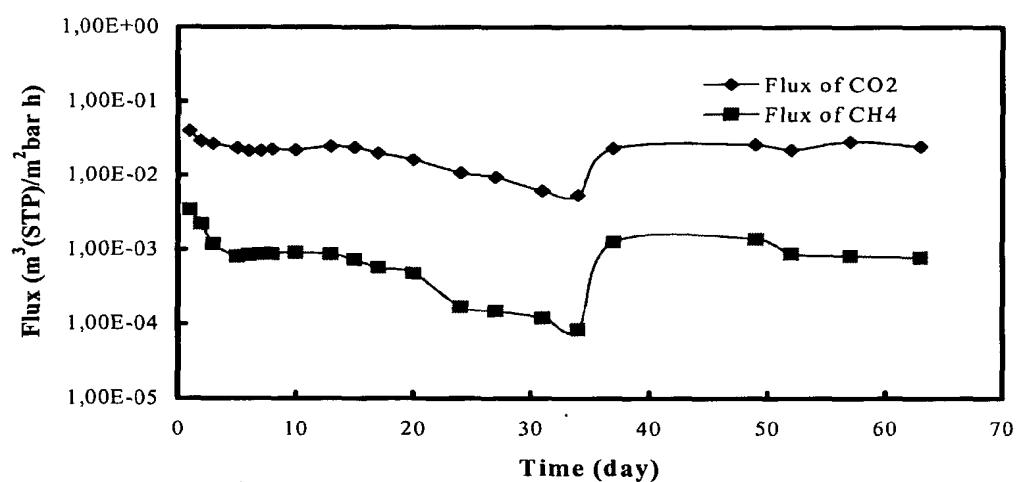


Fig. 3



Perm.flux. of  $\text{CO}_2$  and  $\text{CH}_4$  through the PVAm membrane casted on CA support - after 35 days the membrane is again wetted, and flux is restored.

Fig. 4

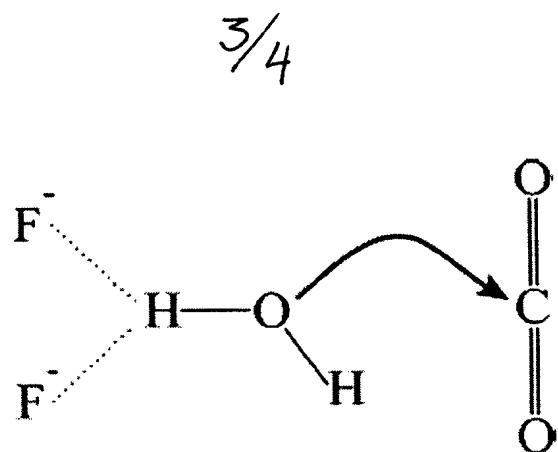


Fig. 5

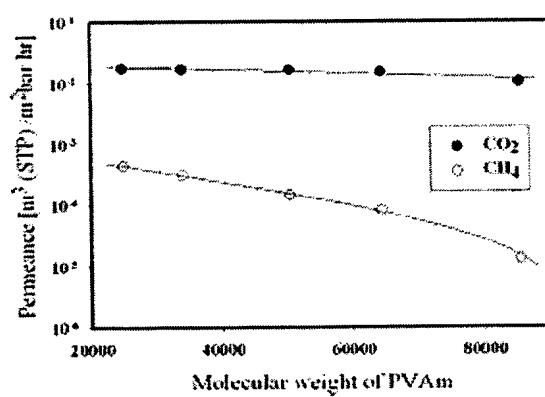


Fig. 6

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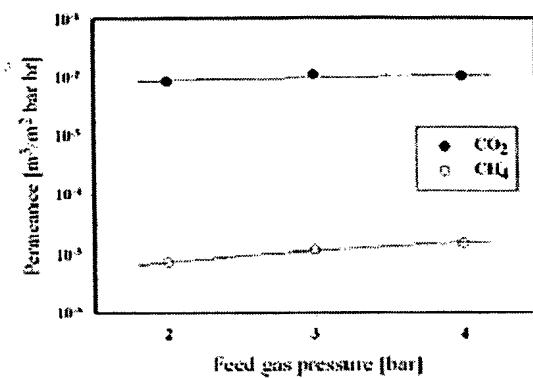


Fig. 7

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 2005/000098

## A. CLASSIFICATION OF SUBJECT MATTER

**IPC7: B01D 53/22, B01D 69/14, B01D 71/60 // B01D179:00**  
 According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

**IPC7: B01D**

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

**SE,DK,FI,NO classes as above**

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**EPO-INTERNAL, WPI DATA, PAJ**

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	Kim, Taek-Joong et al, "Novel Fixed-Site-Carrier Polyvinylamine Membrane for Carbon Dioxide Capture", Journal of Polymer Science: Part B: Polymer Physics, 2004, vol. 42, page 4326 - page 4336  --	1-16
A	US 6315968 B1 (ROBERT QUINN ET AL), 13 November 2001 (13.11.2001)  --	1-16
A	US 6579331 B1 (WIN-SOW WINSTON HO), 17 June 2003 (17.06.2003)  --	1-16

 Further documents are listed in the continuation of Box C. See patent family annex.

\* Special categories of cited documents:

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Date of the actual completion of the international search

11 July 2005

Date of mailing of the international search report

12-07-2005

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**INTERNATIONAL SEARCH REPORT**

International application No.

**PCT/NO 2005/000098****C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<b>DATABASE WPI</b> Week 200306 Derwent Publications Ltd., London, GB; Class A88, AN 2003-060011 & CN 1363414 A (UNIV TIANJIN), 14 August 2002 (2002-08-14) abstract  --	1-16
A	US 5131927 A (BENJAMIN BIKSON ET AL), 21 July 1992 (21.07.1992)  --	1-16
A	Quinn R. et al, "New facilitated transport membranes for the separation of carbon dioxide from hydrogen and methane", Journal of Membrane Science, 1995, vol. 104, page 139 - page 146  -- -----	1-16

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